



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 006 173 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

07.06.2000 Bulletin 2000/23

(21) Application number: **98309774.2**

(22) Date of filing: **30.11.1998**

(51) Int. Cl.⁷: **C10M 141/10**

// (C10M141/10, 129:10,
129:14, 133:12, 133:12, 133:14,
135:02, 133:06, 135:16, 135:18,
137:10), C10N30:08,
C10N30:10, C10N40:08

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

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(54) **Lubricant compositions exhibiting extended oxidation stability**

(57) Use, in a lubricant composition comprising a hydraulic antiwear component and a base oil, of an additive comprising an amine antioxidant and at least one additional antioxidant selected from ashless dithiocarbamate, sulphurised olefin and phenolic, antioxidants to provide a lubricant having improved thermal and oxidation stability.

EP 1 006 173 A1

Description

[0001] The present invention relates to the use of certain additives to extend the thermal stability and oxidation stability of lubricant compositions, and to lubricant compositions exhibiting extended thermal stability and oxidation stability.

[0002] Lubricating compositions for antiwear hydraulic and industrial applications typically contain additive components to impart antiwear performance. Hydraulic grade zinc dialkyldithiophosphates are typically used in this respect. The compositions usually also contain antioxidant components. The compositions have conventionally been formulated using Group I base oils. However, the use of hydrocracked and catalytically dewaxed Group II and Group III base oils is on the increase. The hydrogenation and dewaxing processes involved result in base oils of exceptionally low aromaticity and sulphur level. These Group II and Group III bases have been found to exhibit an improved response to antioxidant components when compared with Group I basestocks. This has led to the thinking that use of Group II and Group III bases could allow the level of antioxidants to be decreased without detriment to the level of antioxidant performance required by end users. However, rather than leading to reduced amounts of antioxidants being used, the advent of Group II and Group III base oils has prompted end users to demand a higher level of antioxidant performance, irrespective of the kind of base oil which is actually used. For example, whereas a performance level of 2000 to 4000 hours in the ASTM D943 thermal oxidation test was previously acceptable, extended performance is now commonly required, for instance a result of 10,000 hours in the ASTM D943 test.

[0003] In accordance with the present invention it has now been found that specific antioxidant components, and combinations thereof, can be blended in lubricant compositions containing hydraulic antiwear components to achieve extended thermal and oxidative stability without formation of sludge. More particularly, the combinations have been found to give improved thermal stability, and thus reduced levels of sludge, when used in Group I, II and III basestocks and increased oxidation stability in Group II, or higher basestocks. These advantageous results enables a variety of base oils to be used in formulating the lubricant composition and, in turn, this allows industrial formulators enhanced flexibility whilst also meeting the now extended performance requirements of end users.

[0004] Accordingly, the present invention provides the use in a lubricant composition comprising a hydraulic antiwear component and a base oil of an additive comprising at least one amine antioxidant and at least one additional antioxidant selected from ashless dithiocarbamate, sulphurized olefin and phenolic, antioxidants to provide a lubricant having improved thermal stability and oxidative stability in all basestock types.

[0005] The performance of the combinations of antioxidants used in accordance with the present invention will vary depending, amongst other things, on the base oil type, the specific combination and the concentration of additive(s), used. In terms of thermal stability the additives used in accordance with the present invention enable formulation of lubricants which may avoid excessive sludge formation after a period of 10 days when the lubricant is tested in accordance with the NOC test and when the base oil used is a Group I basestock. In a preferred embodiment the amount of sludge produced after 10 days in this test is not more than 100 mg/100 ml, preferably not more than 25 mg/100 ml. A 10 day sludge result of less than 10 mg/100 ml is particularly preferred. In terms of oxidation stability the additives used in accordance with the present invention typically enable formulation of lubricants which use a Group II or higher basestock and which give a result of at least 500 minutes, preferably at least 600 minutes, in the RBOT thermal stability test. Thus, the present invention relates to combinations of antioxidants which may be used to achieve good oxidation performance in Group II or higher basestock without derating thermal stability performance when Group I or higher basestock is used, and vice versa.

[0006] The amine used in the present invention is selected from optionally alkylated diphenylamines, phenyl-naphthylamines and mixtures thereof. Examples of such components that may be used in this invention include, but are not limited to, diphenylamine, phenyl- α -naphthylamine, phenyl-beta-naphthylamine, butyldiphenylamine, dibutyldiphenylamine, octyldiphenylamine, dioctyldiphenylamine, nonyldiphenylamine, dinonyldiphenylamine, dioctyldiphenylamine, nonyldiphenylamine, dinonyldiphenylamine, heptyldiphenylamine, diheptyldiphenylamine, methylstyryldiphenylamine, mixed butyl/octyl alkylated diphenylamines, mixed butyl/styryl alkylated diphenylamines, mixed nonyl/ethyl alkylated diphenylamines, mixed octyl/styryl alkylated diphenylamines, mixed ethyl/methylstyryl alkylated diphenylamines, octyl alkylated phenyl- α -naphthylamines and mixed alkylated phenyl- α -naphthylamines. 2,6-di-*t*-butyl- α -dimethylamino-*p*-cresol may also be used.

[0007] Useful amine antioxidants are generally characterized by their nitrogen content and TBN as determined by ASTM D 2896. It is preferred that the nitrogen content of the amine antioxidants be between 3.0 and 7.0 wt% and the TBN be between 100 and 250 mg KOH/g of the neat, i.e. undiluted, component.

[0008] The concentration of amine antioxidant(s) in the finished composition varies depending upon the basestock used, customer requirements and applications. Typically, the total amount of amine antioxidant present in the finished composition is from 0.04 wt% to 0.4 wt%, preferably, from 0.05 wt% to 0.2 wt %.

[0009] The sulphur-containing compounds of the present invention are selected from the group consisting of sulphurized olefins, sulphurized fatty acids, ashless dithiocarbamates, tetraalkylthiuram disulphides and mixtures thereof.

The sulphurized olefins suitable for use in the present invention may be prepared by a number of known methods. They are typically characterized by the type of olefin used in their production and their final sulphur content. High molecular weight olefins (e.g., those having an average molecular weight (Mn) of from about 112 to about 351 g/mole) are preferred. Examples of olefins that may be used include α -olefins, isomerized α -olefins, branched olefins, cyclic olefins, polymeric olefins and mixtures thereof. Examples of α -olefins that may be used include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tricosene, 1-tetracosene, 1-pentacosene and mixtures thereof. α -Olefins may be isomerized before the sulphurization reaction or during the sulphurization reaction. Structural and/or conformational isomers of the α -olefins that contain internal double bonds or branching may also be used. For example, isobutylene is the branched olefin counterpart of the α -olefin 1-butene.

[0010] Sulphur sources that may be used in the sulphurization reaction can include, for example, elemental sulphur, sulphur monochloride, sulphur dichloride, sodium sulphide, sodium polysulphide, and mixtures thereof added together or at different stages of the sulphurization process.

[0011] Unsaturated fatty acids and oils, because of their unsaturation, may also be sulphurized and used in this invention. Examples of fatty acids that may be used include lauroleic acid, myristoleic acid, palmitoleic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linolenic acid, gadoleic acid, arachidonic acid, erucic acid, and mixtures of these. Examples of oils or fats that may be used include corn oil, cottonseed oil, grapeseed oil, olive oil, palm oil, peanut oil, rapeseed oil, safflower seed oil, sesame seed oil, soybean oil, sunflower oil, sunflower seed oil, and combinations thereof.

[0012] Examples of ashless dithiocarbamates that may be used include, but are not limited to, methylene-bis(dialkylidithiocarbamate), ethylene-bis(dialkylidithiocarbamate), and isobutyl disulphide-2,2'-bis(dialkylidithiocarbamate), where the alkyl groups of the dialkylidithiocarbamate can preferably have from 1 to 16 carbons. Examples of preferred ashless dithiocarbamates are methylene-bis(dibutylidithiocarbamate), ethylene-bis(dibutylidithiocarbamate), and isobutyl disulphide-2,2'-bis(dibutylidithiocarbamate). Examples of preferred tetraalkylthiuram disulphides that may be used include tetrabutylthiuram disulphide and tetraoctylthiuram disulphide.

[0013] The concentration of the sulphur-containing compound in the finished composition can vary depending upon the customers' requirements and applications. The compound is typically used in an amount of upto 0.1% by weight, preferably upto 0.05% by weight based on the total weight of the lubricant composition. An important criteria for selecting the concentration of the compound is the sulphur content. The compound should typically deliver between 0.005 wt. % and 0.07 wt. % of sulphur to the finished composition. For example, a sulphurized olefin having 12 wt. % sulphur content should be used between 0.04 wt. % and 0.58 wt. % to deliver between 0.005 wt. % and 0.07 wt. % sulphur to the finished composition. An ashless dithiocarbamate having 30 wt. % sulphur content should be used between 0.02 wt. % and 0.23 wt. % to deliver between 0.005 wt. % and 0.07 wt. % sulphur to the finished composition.

[0014] Another criterion useful for selecting the sulphur-containing compound is the content of active sulphur as determined by ASTM D 1662. The presence of high levels of active sulphur can lead to significant corrosion and sludge problems in the finished lubricant. In a preferred embodiment of the present invention, the level of active sulphur in the compound is below 1.5 wt. % as determined by ASTM D 1662.

[0015] An example of a sulphurized olefin that may be used in this invention would contain approximately 12 wt. % total sulphur content and <1 wt. % active sulphur. Examples of commercially available sulphurized fatty oils or mixtures of sulphurized fatty oils and olefins, that may be used in this invention include those having approximately 9.5 wt. % sulphur content and 1 wt. % active sulphur, approximately 12.5 wt. % sulphur content and 1.5 wt. % active sulphur, and approximately 10 wt. % sulphur content and <1 wt. % active sulphur. An example of an ashless dithiocarbamate that may be used in this invention would be one which has approximately 30 wt. % sulphur from a practical standpoint the sulphur-containing compound should contain a minimum of 8.0 wt% sulphur in order to minimize the amount of additive needed to deliver the required amount of sulphur.

[0016] Mixtures of sulphurized olefins, ashless dithiocarbamates and tetraalkylthiuram disulphides, in varying proportions, may also be used, as long as the desired total sulphur content, and active sulphur content are satisfied.

[0017] Examples of phenolic antioxidants which may be used include hindered phenolics such as 2,6-di-butylphenol, 4-methyl-2,6-di-t-butylphenol, 2,4,6-tributylphenol, 2-t-butylphenol, 2,6-diisopropylphenol, 2-methyl-6-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 4-(N,N-dimethylaminomethyl)-2,6-di-t-butylphenol, 4-ethyl-2,6-di-t-butylphenol, 2-methyl-6-styrylphenol, 2,6-di-styryl-nonylphenol and mixtures thereof. Also useful are methylene bridged alkyl phenols and these may be used singly or in combination with each other or with sterically hindered unbridged phenols. Examples include 4,4'-methylene-bis(2,6-di-butylphenol), 4,4'-methylene-bis(6-t-butyl-o-cresol), 4,4'-methylene-bis(2-t-amyl-o-cresol), 2,2'-methylene-bis(4-methyl-6-t-butylphenol), methylene bridged t-butylphenol mixtures, iso-octyl-3,5-di-butyl-4-hydroxy hydrocinnamate and thiodiethylene-bis(3,5-di-butyl-4-hydroxy)hydrocinnamate. Also useful are mixtures of methylene bridged alkyl phenols such as described in USP 3,211,652. Typically, the phenolic antioxidant will be present in the finished lubricant in an amount of upto 0.4% by weight, preferably upto 0.15% by weight.

[0018] The present invention also provides lubricant compositions, as described herein, comprising a hydraulic antiwear component, a base oil, at least one amine antioxidant and at least one additional antioxidant.

[0019] The antioxidants useful in the present invention are commercially available or may be prepared by the application or adaptation of known techniques.

5 [0020] Usually, the hydraulic antiwear additive used in the composition of the invention is a hydraulic grade zinc dialkyldithiophosphate (ZDDP). "Hydraulic grade" means that the antiwear component is suitable for use in hydraulic applications, particularly with respect to their thermal stability. (ZDDPs) which have insufficient thermal stability tend to degrade rapidly to breakdown products which can be corrosive, in particular towards copper. This is a serious problem as certain hydraulic system components are made of this metal. Furthermore, the breakdown products can cause
10 sludge formation which in turn can result in filter blocking. Thus, not all types of ZDDPs are suitable for use in the present invention. Zinc dihydrocarbyl dithiophosphates which may be used in the present invention are well-known in the art (see for example U.S. Pat. No. 4,101,429). Suitably the zinc dihydrocarbyl dithiophosphate is a zinc dialkyl dithiophosphate typically containing about 4 to about 12 carbon atoms and more commonly about 6 to about 12 carbon atoms in each alkyl group. Preferably each alkyl group contains about 8 to about 12 carbon atoms. Examples of suitable
15 alkyl moieties include butyl, sec-butyl, isobutyl, tert-butyl, pentyl, n-hexyl, sec-hexyl, n-octyl, 2-ethylhexyl, decyl and dodecyl. Preferably each alkyl moiety is 2-ethylhexyl. Zinc dialkyl dithiophosphates of this type are described in European patent application no. 95306722.0 and are commercially available.

[0021] The ZDDP may be used in the lubricant over a broad weight range. It is usual however that the lubricant contains about 0.4 to about 0.9% by weight ZDDP. Preferably, the fluid comprises 0.6% by weight ZDDP.

20 [0022] It is generally possible to characterise those ZDDPs which are useful in the present invention by reference to their overbased to neutral ratio or by their titratable base number (TBN). Useful ZDDPs typically exhibit an overbased to neutral ratio of from 0.3:1 to 2:1, preferably 0.5:1 to 2:1. ZDDPs having an overbased to neutral ratio of about 1:1 are more commonly used. The ratio in question is determined by ^{31}P nmr. In terms of TBN, useful ZDDPs generally exhibit a minimum value of about 10 mgKOH/g and preferably about 12 mgKOH/g. ZDDPs having a TBN of about 15 mgKOH/g
25 are more commonly used. TBN is determined in accordance with ASTM D664.

[0023] Alternatively, it is generally possible to characterise ZDDPs which may be used by reference to the thermal stability of the finished hydraulic fluid in which they are included. Here reference may be made to the ASTM D2619 and CCM "A" thermal stability tests. To meet the requirements of the ASTM D2619 test the finished fluid should give a maximum copper loss of 0.2 mg. To pass the CMC "A" test the finished fluid should give a maximum copper rod rating of 5
30 and a maximum sludge deposit of 25 mg/100 ml. The ASTM D2619 and CCM "A" tests are well known in the art.

[0024] It is possible to further improve the thermal stability of the lubricant composition by post-treatment of the ZDDP component using a zinc alkanoate. Typically the alkanoate is branched on its β -carbon atom. Such components are also described in European patent application no. 95306722.0. The use of zinc octanoate is preferred, especially an overbased zinc octanoate such as zinc octanoate 22% which is commercially available under this designation.

35 [0025] In an embodiment of the invention the amine antioxidant is phenyl- α -naphthylamine or 2,6-di-*t*-butyl- α -dimethylamino-*p*-cresol, alone or each in combination with diphenylamine. Combinations based on phenyl- α -naphthylamine and diphenylamine are preferred.

[0026] Preferred combinations of antioxidants include: phenyl- α -naphthylamine, diphenylamine and an ashless dithiocarbamate, such as methylene-bis(dibutyldithiocarbamate); phenyl- α -naphthylamine, diphenylamine and a phenolic antioxidant, such as 2,6-di-*t*-butylphenol; and phenyl- α -naphthylamine, diphenylamine and a sulphurised olefin, such as one derived from a mixture of C_{16-18} isomerised α -olefins. In these combinations the phenyl- α -naphthylamine may be replaced by 2,6-di-*t*-butyl- α -dimethylamino-*p*-cresol.

[0027] Lubricating oils contemplated for use in this invention include natural lubricating oils, synthetic lubricating oils and mixtures thereof. Suitable lubricating oils also include basestocks obtained by isomerization of synthetic wax
45 and slack wax, as well as basestocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of crude oil. In general, both the natural and synthetic lubricating oils will each have a kinematic viscosity ranging from about $1 \times 10^{-6} \text{ m}^2/\text{s}$ to about $40 \times 10^{-6} \text{ m}^2/\text{s}$ (about 1 to about 40 cSt) at 100°C, although typical applications will require each oil to have a viscosity ranging from about $2 \times 10^{-6} \text{ m}^2/\text{s}$ to about $8 \times 10^{-6} \text{ m}^2/\text{s}$ (about 2 to about 8 cSt) at 100°C.

50 [0028] Natural base oils include animal oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale. The preferred natural base oil is mineral oil.

[0029] The mineral oils useful in this invention include all common mineral oil base stocks. This would include oils that are naphthenic or paraffinic in chemical structure. Oils that are refined by conventional methodology using acid, alkali, and clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulphur dioxide, furfural, dichloroethyl ether, etc. They may be hydrotreated or hydro-refined, dewaxed by chilling or catalytic dewaxing processes, or hydrocracked. The mineral oil may be
55 produced from natural crude sources or be composed of isomerized wax materials or residues of other refining processes.

[0030] Typically the mineral oils will have kinematic viscosities of from $2 \times 10^{-6} \text{ m}^2/\text{s}$ to $12 \times 10^{-6} \text{ m}^2/\text{s}$ (2 cSt to 12 cSt) at 100°C . The preferred mineral oils have kinematic viscosities of from $3 \times 10^{-6} \text{ m}^2/\text{s}$ to $10 \times 10^{-6} \text{ m}^2/\text{s}$ (3 to 10 cSt), and most preferred are those mineral oils with viscosities of $5 \times 10^{-6} \text{ m}^2/\text{s}$ to $9 \times 10^{-6} \text{ m}^2/\text{s}$ (5 to 9 cSt) at 100°C .

[0031] Synthetic lubricating oils useful in this invention include hydrocarbon oils and halo-substituted hydrocarbon oils such as oligomerized, polymerized, and interpolymers of olefins [e.g., polybutylenes, polypropylenes, propylene, isobutylene copolymers, chlorinated polyethylenes, poly(1-hexenes), poly(1-octenes), and mixtures thereof]; alkylbenzenes [e.g., polybutylenes, polypropylenes, propylene, isobutylene copolymers, chlorinated polyethylenes, poly(1-hexenes), poly(1-octenes) and mixtures thereof]; alkylbenzenes [e.g., dodecyl-benzenes, tetradecylbenzenes, dinonyl-benzenes and di(2-ethylhexyl)benzene]; polyphenyls [e.g., biphenyls, terphenyls, alkylated polyphenyls]; and alkylated diphenyl ethers, alkylated diphenyl sulphides, as well as their derivatives, analogs, and homologs thereof, and the like. The preferred synthetic oils are oligomers of α -olefins, particularly oligomers of 1-decene, also known as polyalpha olefins or PAO's.

[0032] Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers, and derivatives thereof where the terminal hydroxyl groups have been modified by esterification or etherification. This class of synthetic oils is exemplified by: polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polypropylene glycol having a molecular weight of 100-1500); and mono- and poly-carboxylic esters thereof (e.g., the acetic acid esters, mixed C_3 - C_8 fatty acid esters, and C_{12} oxo acid diester of tetraethylene glycol).

[0033] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids and alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoethers and propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl isophthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid. A preferred type of oil from this class of synthetic oils are adipates of C_4 to C_{12} alcohols.

[0034] Esters useful as synthetic lubricating oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane pentaerythritol, dipentaerythritol and tripentaerythritol.

[0035] Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. These oils include tetra-ethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxyl)-disiloxane, poly(dimethyl)-siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus containing acids (e.g., tricresyl phosphate, trioctylphosphate, and diethyl ester of decyl-phosphonic acid), polymeric tetra-hydrofurans and poly- α -olefins.

[0036] The lubricating base oils may be derived from refined, re-refined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Re-refined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These re-refined oils are also known as reclaimed or reprocessed oils and are often additionally processed by techniques for removal of spent additives and oils breakdown products. White oils, as taught in U.S. 5,736,490 may also be used as the base oil, especially for turbine applications.

[0037] In an embodiment of the invention the base oil is a Group I, Group II or Group III base oil. The use of Group II or Group III base oils is preferred.

[0038] The American Petroleum Institute has categorized these different basestock types as follows: Group I, $>0.03 \text{ wt}\%$ sulphur, and/or $<90 \text{ vol}\%$ saturates, viscosity index between 80 and 120; Group II, $\leq 0.03 \text{ wt}\%$ sulphur, and $\geq 90 \text{ vol}\%$ saturates, viscosity index between 80 and 120; Group III, $\leq 0.03 \text{ wt}\%$ sulphur, and $\geq 90 \text{ vol}\%$ saturates, viscosity index >120 ; Group IV, all polyalphaolefins. Hydrotreated basestocks and catalytically dewaxed basestocks, because of their low sulphur and aromatics content, generally fall into the Group II and Group III categories. Polyalphaolefins (Group IV basestocks) are synthetic base oils prepared from various α -olefins and are substantially free of sulphur and aromatics.

[0039] The lubricant composition of the present invention may be prepared by simple blending of the various com-

ponents with a suitable base oil.

[0040] For the sake of convenience, and in another embodiment of the present invention, the additive components used in practice of this invention may be provided as a concentrate for formulation into a lubricant composition ready for use.

5 [0041] The concentrate may comprise, in addition to the fluid components, a solvent or diluent for the fluid components. The solvent or diluent should be miscible with and/or capable of dissolving in the base oil to which the concentrate is to be added. Suitable solvents and diluents are well known. The solvent or diluent may be the base oil of the lubricating oil composition itself. The concentrate may suitably include any of the conventional additives used in lubricating oils compositions. The proportions of each component in the concentrate are controlled by the intended degree of dilution, though top treatment of the formulated fluid is possible.

10 [0042] Other additives commonly used in lubricants/fluids for turbine, antiwear hydraulic and industrial applications may be included in the compositions or concentrates of the present invention. These include demulsifiers, corrosion inhibitors, dispersants, sulphur- and/or phosphorus-containing antiwear agents and rust inhibitors. These additives, when present, are used in amounts conventionally used in such applications. Some additives may be included in the concentrate and some added to the fully formulated lubricant/fluid as a top-treat.

15 [0043] The invention will now be illustrated by the following Examples that are not intended to limit the scope of the invention in any way.

EXAMPLES

20 [0044] A lubricant composition was prepared by blending components in the proportions specified in the following table.

25

Component	% by weight
Corrosion inhibitor	0.0085
Detergent	0.050
30 Rust inhibitor	0.051
Phenolic antioxidant	0.013
Demulsifier	0.0064
35 Process oil	0.0111
*ZDDP	0.510
Base oil	Balance to 100%

40 [0045] The ZDDP was zinc di(2-ethylhexyl)dithiophosphate.

[0046] The base oil used was either a Group I or Group II base oil. Further details of this are given in the following table.

45 [0047] To this lubricant composition was blended various additional components at the concentration(s) listed in the following table. The resulting lubricant compositions were then tested in the CCM "A", NOC and RBOT tests. The results are also shown in the following table.

50

55

Component (% by weight)	RUN											
	1	2	3	4	5	6	7	8	9	10	11	12
Diphenylamine	-	0.1	0.1	-	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Phenyl- α -naphthylamine	-	-	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphurised phenolic	-	-	-	-	-	-	-	0.1	0.1	0.05	0.05	0.1
2,6-di-t-butylphenol	-	-	-	-	-	-	-	-	-	-	-	-
Sulphurised olefin	-	-	-	-	-	-	-	-	-	-	-	-
Ashless dithiocarbonate	-	-	-	-	-	-	-	-	-	-	-	-
Base oil type	I	I	II	I	II	I	II	I	II	I	II	I
CCM "A" Cu rod rating	1	I	I	1	1	1	1	1	1	1	1	1
NOC sludge after 10 days (mg)	BF	4.4	2.0	313	2.8	BF	3.6	BF	12.1	BF	3.6	BF
RBOT (minutes)	274	287	336	340	465	365	570	390	629	375	508	335

BF - Blocked Filter

RUN											
Component (% by weight)	13	14	15	16	17	18	19	20	21	22	23
Diphenylamine	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Phenyl- α -naphthylamine	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphurised phenolic	0.1	0.05	0.05	-	-	-	-	-	-	-	-
2,6-di-t-butylphenol	-	-	-	-	-	-	-	0.1	0.1	-	-
Sulphurised olefin	-	-	-	-	-	-	-	-	-	0.05	0.05
Ashless dithiocarbonate	-	-	-	0.05	0.05	0.025	0.025	-	-	-	-
Base oil type	II	I	II	I	II	I	II	I	II	I	II
CCM "A" Cu rod rating	1	1	1	1	1	1	1	1	1	2	1
NOC sludge after 10 days (mg)	2.2	BF	4.7	82.4	14.3	93.4	6.7	4.0	4.3	48.2	16.0
RBOT (minutes)	538	350	616	373	661	378	600	391	525	378	677

NOTES

5 The Group I base oil was Texaco ISO 46. The Group II base oil was RLOP
ISO 46. In Runs 8-11 the sulphurised phenolic compound was thioethylene-bis(3,5-
10 di-t-butyl-4-hydroxyhydro cinnamate). In Runs 12-15 a different sulphurised
phenolic compound was used. The sulphurised olefin was a commercially available
one derived from a mixture of C₁₆₋₁₈ isomerised α -olefins. The ashless
dithiocarbamate was methylene-bis(dibutyldithiocarbamate).

15 The NOC test was carried out as follows. To each of four 50 ml beakers
added 45 g of test oil and an eighth length of a Copper/Iron coil used for ASTM
D943. The beakers were stored in an oven at 140°C and after 4, 6, 8 and 10 days, the
20 beaker removed from the oven and the test oil analysed [for colour (ASTM D1500)]
and sludge content (0.8mm filter). The 10 day sludge results are given as mg sludge
per 100 ml oil.

25 Thermal stability was also assessed using the Cincinnati Milacron Thermal
Stability test, procedure A (CCM "A") which runs for 168 hours at 135°C with
copper and iron rods.

30 The RBOT was performed in accordance with ASTM D2272. The test
measures oxidation life in minutes and can be used as an indicator of oxidation
performance in the ASTM D943 (TOST) test.

35 In the table low sludge in the NOC test after 10 days using a Group I
basestock and a high RBOT result (greater than 500 minutes) using a Group II
basestock are illustrative of antioxidants which impart the desired combination of
40 thermal stability and oxidation stability.

 In Run 1 the additive pack is used in a Group I basestock. A significant
amount of sludge is formed resulting in filter blocking in the NOC test. In Runs 2-15
45 various antioxidants and combinations of antioxidants are employed. However, in
these Runs either filter blocking occurs when a Group I basestock is used and/or the
RBOT results are insufficiently low (less than 500 minutes) when a Group II
50 basestock is used. The antioxidant(s) used in Runs 2-15 do not provide the desired
combination of thermal stability (in a Group I basestock) and oxidative stability (in a

Group II basestock).

5 In contrast, Runs 16-23 are illustrative of the present invention. In these Runs antioxidant combinations are employed which give extended oxidation stability in the Group II basestock without excessive sludge formation when a Group I basestock
10 is used. The results for Runs 16-19 show that addition of an ashless dithiocarbamate can extend the oxidative stability of the combination diphenylamine and phenyl- α -naphthylamine without excessive sludge formation. The same is true for the use of
15 2,6-di-t-butyl phenol (Runs 20 and 21) and sulphurised olefin (Runs 22 and 23). The results for these Runs suggest that there is some kind of synergy between the individual antioxidants used.

20 These results confirm that the selection of antioxidants in accordance with the present invention provides antioxidant system that allows extended oxidation stability in Group II basestocks without excessive sludge formation when a Group I
25 or II basestock is used.

30 Claims

1. Use, in a lubricant composition comprising a hydraulic antiwear component and a base oil, of an additive comprising an amine antioxidant and at least one additional antioxidant selected from ashless dithiocarbamate, sulphurised
35 olefin and phenolic, antioxidants to provide a lubricant having improved thermal and oxidation stability.
2. Use according to claim 1, wherein the antiwear component is a hydraulic grade zinc dialkyldithiophosphate.
3. Use according to claim 1 or claim 2, wherein the base oil is a Group I basestock.
- 40 4. Use according to claim 1 or 2, wherein the base oil is a Group II or Group III basestock.
5. Use according to any one of claims 1 to 4, wherein the additive comprises diphenylamine and phenyl- α -naphthylamine.
- 45 6. Use according to any one of claims 1 to 4, wherein the additive comprises diphenylamine and 2,6-di-t-butyl- α -dimethylamino-p-cresol.
7. Use according to any one of claims 1 to 6, wherein the phenolic antioxidant is 2,6-di-t-butylphenol.
- 50 8. Use according to any one of claims 1 to 6, wherein the sulphurised olefin is derived from a mixture of C₁₆₋₁₈ isomerised α -olefins.
9. Use according to any one of claims 1 to 6, wherein the ashless dithiocarbamate is methylene-bis(di-butylthiocarbamate).
- 55 10. Use according to any one of the preceding claims, wherein the total amount of amine antioxidant is from 0.04 to 0.4 wt% based on the total weight of the lubricant.

EP 1 006 173 A1

11. A lubricant composition comprising a hydraulic antiwear component, a base oil, at least one amine antioxidant and at least one antioxidant selected from ashless dithiocarbamate, sulphurised olefin and phenolic, antioxidants.

12. A composition according to claim 11, wherein the additive is as defined in any one of claims 5 to 9.

13. A composition according to claim 11 or 12, wherein the total amount of amine antioxidant is from 0.04 to 0.4 % by weight based on the total weight of the composition.

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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 9774

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EPO FORM 1503 03.92 (P4/C01)



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EUROPEAN SEARCH REPORT

Application Number
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